

Hardness profile and activation hardness for rotational isomerization processes.

1. Application to nitrous acid and hydrogen persulfide

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A theoretical study of the conformational dependence upon internal rotation of molecular hardness and its correlation with the torsional potential energy is performed for two representative molecules that present rotational isomerization. In order to characterize such correlation, the hardness and potential energy along a torsional angle θ are expressed as functional forms ($H[\theta]$ and $V[\theta]$, respectively) of a reduced variable $w(\theta) = 1/2(1 - \cos \theta)$ that gives the statistical weight of the reference conformations along θ . Correlations among $H[\theta]$ and $V[\theta]$ are then found by splitting $H[\theta]$ and $V[\theta]$ into symmetric and asymmetric parts. This leads to a formula defining the activation hardness in terms of the activation energy and the energy difference between two reference conformations. From this formula, we perform a qualitative analysis to characterize the conditions under which the principle of maximum hardness (PMH) holds. The procedure is used to analyze HF ab initio results of the intern